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The Influence of the Exchange-Correlation Functional on the Non-Interacting Kinetic Energy and Its Implications for Orbital-Free Density Functional Approximations

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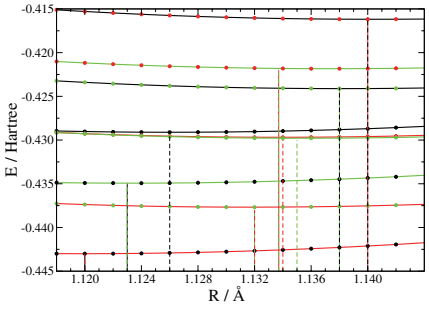
Abstract: In this work it is shown that the kinetic energy and the exchange-correlation energy are mutual dependent on each other. This aspect is first derived in an orbital-free context. It is shown that the total Fermi potential depends on the density only, the individual parts, the Pauli kinetic energy and the exchange-correlation energy, however, are orbital dependent and as such mutually influence each other. The numerical investigation is performed for the orbital-based non-interacting Kohn-Sham system in order to avoid additional effects due to further approximations of the kinetic energy. The numerical influence of the exchange-correlation functional on the non-interacting kinetic energy is shown to be of the order of a few Hartrees. For chemical purposes, however, the energetic performance as a function of the nuclear coordinates is much more important than total energies. Therefore, the effect on the bond dissociation curve was studied exemplarily for the carbon monoxide. The data reveals that, the mutual influence between the exchange- correlation functional and the kinetic energy has a significant influence on bond dissociation energies and bond distances. Therefore, the effect of the exchange-correlation treatment must be considered in the design of orbital-free density functional approximations for the kinetic energy.



Key Words: Density functional approximation; Density functional approximation; Kinetic energy functional; Exchange-correlation functional; Bond dissociation energy; Bond distance

1 Introduction

Functional development for the non-interacting kinetic energy [1–4] has recently regained in interest, as two major research lines: orbital-free density functional theory and embedding approaches benefit from an appropriate functional description. The first kinetic energy functional dates back to Thomas and Fermi [5,6] in 1928, even much earlier than the theoretical foundations of density functional theory (DFT) led by Hohenberg and Kohn in their seminal paper [7]. However, finding appropriate density-based functional approximations for the kinetic energy has been proven to be severely difficult. Thus, the orbital-based Kohn-Sham method (KS) [8] became the most popular variant of density functional theory. A big issue in the design of kinetic energy functionals is to avoid the variationally obtained electron density to fall into the structureless bosonic-like solution, a well-known defect that is inherently related to the problem of imposing proper N-representability conditions on the functional [9–11].

First work was done using conventional gradient expansion techniques [5,6,12–15] and extended by generalized gradient approximations motivated by conjoint arguments [16–18] or the fulfillment of additional constraints [19–21]. But also information-theory motivated functionals [22–24], functionals based on response theory [25,26], and expansions in terms of moment densities [27] were studied. In practice it is very difficult to find suitable kinetic energy functional approximations, which are able to yield electron densities with proper N-fermionic behavior, like for example the atomic shell structure of the radial electron density [28–31]. This failure is attributed to an insufficient incorporation of the Pauli exclusion

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principle [21,32,33] in the Pauli kinetic energy and the corresponding Pauli potential [34]. Both terms were intensively studied in the literature [35–43] as they represent the only unknown part of the kinetic energy functional and the corresponding potential, respectively. Recently, an ad hoc formalism how to construct approximations for the Pauli potential, which are able to yield properly structured electron densities [44–47] has been presented. A generalized method how to design functional approximations with specified functional derivatives [48] has been published consecutively.

This work focuses on another important aspect for the design of kinetic energy density functionals: its implicit orbital-dependence. While the explicit orbital-dependence for the kinetic energy is obvious, namely finding a density-based approximation for the kinetic energy which is known in terms of orbitals, the implicit orbital-dependence of the kinetic energy is more subtle. This additional dependence is due to the fact that only the total Fermi potential [49] is a pure density functional, whereas its both components: the kinetic and the exchange-correlation part, depend on the chosen system, and are thus, orbital-dependent. Whereas this aspect is well-known for the non-interacting *versus* the real interacting system [50], the same applies to the non-interacting Kohn-Sham system itself, due to the different treatment of the exchange-correlation effects when using different functionals. In fact, the intense relationship between the kinetic and the exchange energy density is known since long time and has lead to the conjoint hypothesis, which was intensively applied in the development of kinetic energy density functional approximations by employing the same enhancement factor for both terms: the kinetic and the exchange component [16–18]. Here, however, the implicit orbital-dependence is tested or the exact non-interacting kinetic energy. Therefore, the Section 2 deals with the origin of the implicit orbital-dependence for the exact non-interacting kinetic energy, formally derived within an orbital-free formalism, but the numerical data presented in the Section 3 is taken from a conventional KS calculation.

2 Theory

It is a well-known fact that for density functional approximations the exchange and correlation terms are usually treated together as both parts significantly influence one another [33,51]. The aim of this work is to show that the same applies to the kinetic energy if one aims to target orbital-free density functional calculations. The following section deals with the orbital-free derivation of the above aspect. In contrast, the numerical investigation is carried out with the help of the KS system in order to exclude errors originating from the kinetic energy functional expression itself.

The Hohenberg-Kohn theorems [7] provide the theoretical foundation for a direct minimization of the total electronic energy of the system E with respect to its electron density $\rho(\vec{r})$ subject to the constraint that the latter stays appropriately normalized to the number of electrons N ($0 = \mu[\int \rho(\vec{r})\,\mathrm{d}\vec{r} - N]$):

$$0 = \frac{\delta E[\rho]}{\delta \rho} - \mu, \tag{1}$$

whereby the introduced Lagrange multiplier μ equals the chemical potential [51]. It is possible to split the total energy of the system into energy terms which are independent of the particles nature, and consequently also apply to boson-type particles $E_\mathrm{B}[\rho]$, and the remaining energy terms which account for the fermionic nature of the electrons $E_\mathrm{F}[\rho]$:

$$E[\rho] = E_\mathrm{B}[\rho] + E_\mathrm{F}[\rho] \tag{2}$$

with:

$$E_\mathrm{B}[\rho] = T_\mathrm{W}[\rho] + E_\mathrm{Z}[\rho] + E_\mathrm{H}[\rho] \tag{3}$$

and:

$$E_\mathrm{F}[\rho] = T_\mathrm{P}[\rho] + E_\mathrm{XC}[\rho]. \tag{4}$$

Strictly speaking, the exact correlation functional is not a purely fermionic effect as it counterbalances the simple scaling behavior of the non-interacting kinetic energy resulting from the choice of the KS system [52]. For simplicity, however, the label XC is kept as notation. Hereby, the von Weizsäcker kinetic energy $T_\mathrm{W}[\rho]$ [12], the electron-nuclear attraction $E_\mathrm{Z}[\rho]$ (for a system with M nuclei), and the Hartree repulsion energy $E_\mathrm{H}[\rho]$ belong to the bosonic-like type functionals, and thus, are known as explicit density functionals:

$$T_\mathrm{W}[\rho] = \int \frac{1}{8}\frac{(\nabla\rho(\vec{r}))^2}{\rho(\vec{r})}\,\mathrm{d}\vec{r}, \tag{5}$$

$$E_\mathrm{Z}[\rho] = -\sum_A^M Z_A \int \frac{\rho(\vec{r})}{|R_A - \vec{r}|}\,\mathrm{d}\vec{r}, \tag{6}$$

$$E_\mathrm{H}[\rho] = \frac{1}{2}\int\int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|}\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}', \tag{7}$$

Note that ground-state functionals of the bosonic-type can always be derived by placing the appropriately normalized square root of the electron density into the corresponding orbital-dependent wavefunction expressions. In contrast, the fermionic parts, the Pauli kinetic energy $T_\mathrm{P}[\rho]$ and the exchange-correlation energy $E_\mathrm{XC}[\rho]$, are unknown and must be approximated in density functional calculations. By knowledge of the remaining unknown fermionic terms, the electron density could directly be determined from the Euler Eq.(1), whereby each potential v_k is the functional derivative of the corresponding density functional $v_k = \delta E_k/\delta\rho$ for the energy terms in Eq.(2):

$$0 = v_\mathrm{W}([\rho];\vec{r}) + v_\mathrm{Z}([\rho];\vec{r}) + v_\mathrm{H}([\rho];\vec{r}) + v_\mathrm{F}([\rho];\vec{r}) - \mu \tag{8}$$

Notice, that the Fermi-potential v_F, which is defined as the sum of the kinetic and potential contribution originating from the unknown fermionic energy terms:

$$v_\mathrm{F}([\rho];\vec{r}) = v_\mathrm{P}([\{\Phi_i\}];\vec{r}) + v_\mathrm{XC}([\{\Phi_i\}];\vec{r}) \tag{9}$$

is an explicit density functional and can, at least at the solution point, trivially be obtained from Eq.(8). In practice, the individual parts, however, are not pure density functionals, they have an additional orbital dependence.

At the solution point the formal functional derivative of the Pauli kinetic energy, the so-called Pauli potential, can for a single Slater determinant wavefunction (Hartree-Fock (HF) or Kohn-Sham (KS)) be expressed in terms of the eigenvalues ϵ_i and eigenfunctions $\Phi_i(\vec{r})$ of the corresponding single particle operator[35,53]:

$$v_{\mathrm{P}}([\{\Phi_i\}];\vec{r}) = \frac{\tau(\vec{r}) - t_{\mathrm{W}}(\vec{r})}{\rho(\vec{r})} + \sum_i^{\mathrm{occ}} (\mu - \epsilon_i) \frac{|\Phi_i(\vec{r})|^2}{\rho(\vec{r})} \quad (10)$$

with $\tau(\vec{r}) = 1/2 \sum_i^{\mathrm{occ}} |\nabla\Phi_i(\vec{r})|^2$ being the positive kinetic energy density, $t_{\mathrm{W}}(\vec{r}) = 1/8|\nabla\rho(\vec{r})|^2/\rho(\vec{r})$ being the Weizsäcker kinetic energy density. At the solution point, cf. Eq.(8), the exchange-correlation potential is then numerically equivalent to:

$$v_{\mathrm{XC}}([\{\Phi_i\}];\vec{r}) = \mu - v_{\mathrm{W}}([\rho];\vec{r}) - v_{\mathrm{Z}}([\rho];\vec{r}) - v_{\mathrm{H}}([\rho];\vec{r}) - \frac{\tau(\vec{r}) - t_{\mathrm{W}}(\vec{r})}{\rho(\vec{r})} - \sum_i (\mu - \epsilon_i) \frac{|\Phi_i(\vec{r})|^2}{\rho(\vec{r})} \quad (11)$$

immediately revealing the mutual orbital dependence of the pair $v_{\mathrm{P}}([\{\Phi_i\}];\vec{r})$, $v_{\mathrm{XC}}([\{\Phi_i\}];\vec{r})$. For example, the Pauli potential for the real interacting system described by HF theory is obtained from the HF eigenfunctions and eigenvalues. In that case, the corresponding exchange-correlation potential (it is a matter of taste whether one would like to call the remaining piece a pure exchange or an exchange-correlation potential, both versions exists in the literature [49,54,55]) is the Slater potential [56]. On the other hand it is well-known that the Slater potential is different from the KS potential yielding the HF electron density [54,55,57], in which case the eigenfunctions of the non-interacting KS system are used to evaluate the Pauli potential.

This is caused by the implicit orbital-dependence of the individual pieces $v_{\mathrm{P}}([\{\Phi_i\}];\vec{r})$ and $v_{\mathrm{XC}}([\{\Phi_i\}];\vec{r})$, whereas their sum is orbital-independent, and, thus equal for the HF and the KS system [49]. Even if the individual components $v_{\mathrm{P}}([\{\Phi_i\}];\vec{r})$ and $v_{\mathrm{XC}}([\{\Phi_i\}];\vec{r})$ could be modeled correctly by density based approximations, those approximations must be different for the interacting and the non-interacting systems. In the present case, the impact on the potentials is large, as the KS and the Slater potential significantly differ from one another. The impact on the kinetic energy however, is surprisingly small as shown by the work of Görling and Ernzerhof [58]. In this study, the impact on the kinetic energy for the non-interacting KS system itself for various treatments of exchange-correlation effects is investigated. The origin of that dependence is as in the previous example due to the splitting of the total Fermi potential into a kinetic and an exchange-correlation contribution and the mutual influence on one another.

In the KS formalism [8] the non-interacting kinetic energy is given explicitly in terms of orbitals:

$$T_{\mathrm{s}}[\{\Phi_i(\vec{r})\}] = \sum_i^{\mathrm{occ}} \int \Phi_i^*(\vec{r}) \left(-\frac{1}{2}\nabla_i^2 \Phi_i(\vec{r})\right) \mathrm{d}\vec{r} \quad (12)$$

with $\Phi_i(\vec{r})$ obeying the KS eigenvalue equation:

$$-\frac{1}{2}\nabla^2\Phi_i(\vec{r}) + v_{\mathrm{eff}}([\rho];\vec{r})\Phi_i(\vec{r}) = \epsilon_i\Phi_i(\vec{r}), \quad (13)$$

whereby the local multiplicative effective potential is given by:

$$v_{\mathrm{eff}}([\rho];\vec{r}) = v_{\mathrm{Z}}([\rho];\vec{r}) + v_{\mathrm{H}}([\rho];\vec{r}) + v_{\mathrm{XC}}([\{\Phi_i\}];\vec{r}). \quad (14)$$

Subtracting $v_{\mathrm{eff}}([\rho];\vec{r})\Phi_i(\vec{r})$ from Eq.(13), multiplying with $\Phi_i^*(\vec{r})$ from the left, and inserting into Eq.(12) yields:

$$T_{\mathrm{s}}[\rho] = \int \rho(\vec{r}) \left[-v_{\mathrm{eff}}([\rho];\vec{r})\right] \mathrm{d}\vec{r} + \sum_i^{\mathrm{occ}} \epsilon_i. \quad (15)$$

The above expression is formally a pure density functional for the non-interacting kinetic energy (as required in orbital-free density functional theory). However, since it was obtained in the spirit of the KS formalism, it still requires solving for the N independent particles *via* Eq.(14) in order to obtain the eigenvalues ϵ_i. From Eqs.(14) and (15) the direct influence of $v_{\mathrm{XC}}([\{\Phi_i\}];\vec{r})$ on $T_{\mathrm{s}}[\rho]$ is immediately visible, which is the major aspect of this work. The order of magnitude for this dependence is illustrated in the following section.

3 Results and discussion

KS calculations have been performed with the Gaussian program[59] for the atoms He, Ne, Ar, Kr, and the CO molecule. The cc-pVQZ basis set[60] was employed and the following exchange-correlation functionals were tested: LDA[8], Xα[61], PW91[62,63], PBE[64], VSXC[65], revTPSS[66], and B3LYP[67].

Fig.1 compiles the differences of the non-interacting kinetic energy with respect to the values obtained from LDA $\Delta T_{\mathrm{s}} = T_{\mathrm{s}}^{\mathrm{XC}} - T_{\mathrm{s}}^{\mathrm{LDA}}$ using various functionals for He, Ne, Ar, and Kr. As can been seen from the data ΔT_{s} increases with increasing number of electrons in the system and is of the order of a few Hartree. Recall that the correlation contribution to the kinetic energy, which is the difference between the interacting HF kinetic energy and the non-interacting KS kinetic energy (yielding the HF density) is of the order of a few millihartrees only [58]. Therefore, the influence of the exchange-correlation functional on the non-interacting kinetic energy is of high significance and should be considered when searching for suitable density-based functional approximations for the kinetic energy.

From a chemists viewpoint, more crucial than the influence on the total energy, is the influence on bond dissociation energies and bond distances, which is due to the fact that the entanglement between the kinetic and the potential energy depends on the bond nuclear coordinates. In case of a dimer, the total kinetic energy as a function of bond distance R:

$$E(R) = T_{\mathrm{s}}^{\mathrm{XC}}(R) + V^{\mathrm{XC}}(R). \quad (16)$$

Table 1 Bond distances in for CO using LDA, Xα, PW91, PBE, VSXC, revTPSS, and B3LYP (shown in the diagonal line) as well as their combinations using T_s^{XC} and the remaining total potential energy V^{XC} using the indicated XC functional.

	V^{XC}						
T_s^{XC}	LDA	Xα	PW91	PBE	VSXC	revTPSS	B3LYP
LDA	1.138 (0.0)	1.135 (0.3)	1.150(1.2)	1.148 (1.0)	1.134(−0.1)	1.141 (0.4)	1.117(−1.2)
Xα	1.129(−0.3)	1.126 (0.0)	1.140(0.9)	1.138 (0.7)	1.125(−0.3)	1.132 (0.1)	1.109(−1.4)
PW91	1.123(−1.3)	1.120(−0.9)	1.134(0.0)	1.132(−0.3)	1.119(−1.2)	1.126(−0.7)	1.104(−2.2)
PBE	1.126(−0.9)	1.123(−1.1)	1.137(0.3)	1.135 (0.0)	1.122(−0.9)	1.129(−0.5)	1.107(−2.0)
VSXC	1.135 (0.1)	1.132 (0.3)	1.147(1.4)	1.145 (1.0)	1.131 (0.0)	1.138 (0.5)	1.115(−1.1)
revTPSS	1.131(−0.4)	1.128(−0.2)	1.143(0.8)	1.141(−0.1)	1.127(−0.5)	1.134 (0.0)	1.111(−1.6)
B3LYP	1.146 (1.3)	1.143 (1.6)	1.150(1.9)	1.150 (1.8)	1.141 (1.2)	1.149 (1.7)	1.124 (0.0)

The relative error in % with respect to the mean value of the two functional types is given in parenthesis.

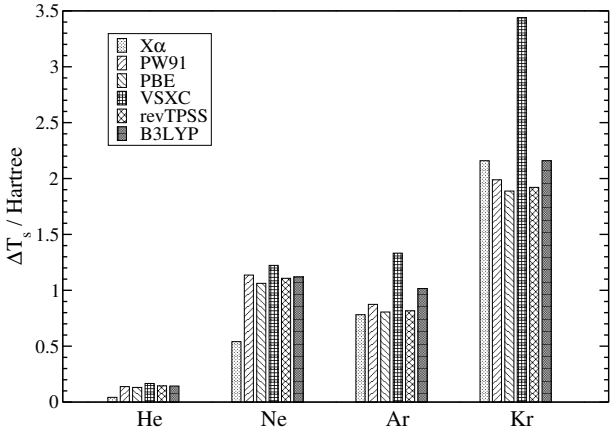

Fig.1 Differences $\Delta T_s = T_s^{XC} - T_s^{LDA}$ (in Hartree) for XC being Xα, PW91, PBE, VSXC, revTPSS, and B3LYP for He, Ne, Ar, and Kr, respectively.

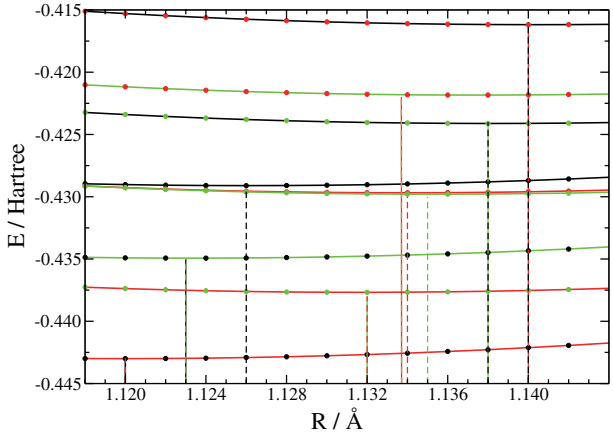

Fig.2 Bond dissociation energy curves *versus* distance for the CO molecule calculated with XC being Xα (shown in black), PW91 (shown in red), and PBE (shown in green), and various combinations $T_s^{XC}(R)$ and $V^{XC}(R)$.

The color code of the line refers to the kinetic energy and the color code of the symbols stands for the potential energy component (black: Xα, red: PW91, green: PBE). Most of the mixed bond dissociation energy curves exhibit minima that lie outside the pure functional range.

contains a kinetic component $T_s^{XC}(R)$ and a potential energy $V^{XC}(R)$ (including the nuclear repulsion). As shown before, both terms depend on the chosen XC functional. If the kinetic energy and the exchange-correlation energy would be sufficiently independent of one another (and in the current design of kinetic energy functionals they are treated as if), then the kinetic and potential energy terms as a function of bond distances should roughly be interchangeable for two separate KS calculations obtained with different exchange-correlation functionals. Meaning that the sum of kinetic energy (as a function of bond distance) obtained from an LDA calculation and the remaining potential energy from a PBE calculation should somehow perform as a (possibly weighted) average of the two functionals. To test this assumption, all 49 combinations using LDA[8], Xα[61], PW91[62,63], PBE[64], VSXC[65], revTPSS[66], and B3LYP[67] have been employed in order to obtain the corresponding total energy curves. The bond dissociation curves (total energy of the molecule minus the total energy of the fragments) as a function of bond distance are exemplarily shown for the combinations of Xα[61], PW91[62,63], and PBE[64], see Fig.2. The bond distances and dissociation energies for the complete set are compiled in Tables 1 and 2, respectively. As can be seen from Fig.2 the energy minima of the combined functional curves do in general not lie between the minima of the pure (realizable) functional calculations. The same trend is observed for the larger test set, cf. Table 1. Obviously, the mutual influence of the kinetic energy and the exchange-correlation functional is large as it shifts the energy minimum beyond the weighted average of the individual energy minima. Therefore, in the design and performance of kinetic energy functionals, the exchange-correlation component is of crucial importance as the final results significantly depend upon it. Finally, the performance of a kinetic energy functional must be documented with the corresponding exchange-correlation component as its stand-alone performance is not reproducible and thus, of no value.

Notice that, the splitting for the combined data curves with respect to the dissociation energies is even much larger than for the bond distances itself, cf. Table 2. Due to the significant influence of the kinetic and exchange-correlation component on each other, the virial ratio is no more fulfilled for various combinations and consequently, for the corresponding kinetic

Table 2 Bond dissociation energies (in Hartrees) for CO using LDA, Xα, PW91, PBE, VSXC, revTPSS, and B3LYP (shown in the diagonal line) as well as their combinations using T_s^{XC} and the remaining total potential energy V using the indicated XC functional.

	V^{XC}						
T_s^{XC}	LDA	Xα	PW91	PBE	VSXC	revTPSS	B3LYP
LDA	−0.419 (0.0)	−0.385(−9.3)	−0.372(−12.2)	−0.380(−10.4)	−0.326(−21.5)	−0.332(−19.3)	−0.287(−30.5)
Xα	−0.463 (9.2)	−0.429 (0.0)	−0.416 (−3.1)	−0.424 (−1.2)	−0.371(−11.9)	−0.377 (−9.7)	−0.332(−20.6)
PW91	−0.477(13.5)	−0.443 (3.2)	−0.430 (0.0)	−0.438 (1.8)	−0.384 (−8.7)	−0.390 (−6.4)	−0.347(−17.2)
PBE	−0.469(10.5)	−0.435(−2.8)	−0.422 (−1.8)	−0.430 (0.0)	−0.376(−10.6)	−0.382 (−8.4)	−0.339(−19.2)
VSXC	−0.505(21.5)	−0.471 (11.9)	−0.458 (10.7)	−0.466 (10.7)	−0.412 (0.0)	−0.418 (2.5)	−0.374 (−8.9)
revTPSS	−0.491(19.3)	−0.457 (9.6)	−0.444 (6.5)	−0.452 (2.3)	−0.398 (−2.4)	−0.404 (0.0)	−0.360(−11.3)
B3LYP	−0.540(30.6)	−0.506 (20.9)	−0.494 (17.9)	−0.502 (19.8)	−0.447 (9.0)	−0.454 (11.7)	−0.408 (0.0)

The relative error in % with respect to the mean value of the two functional types is given in parenthesis.

energy density functional when trained to reproduce the original KS data.

The above analysis shows that the influence of the exchange-correlation functional on the kinetic energy (even if treated correctly within the KS approach) is beyond the order of chemical accuracy. An uncorrelated treatment of individual kinetic and potential components may significantly alter chemical bonding concepts as it severely influences bond distances and dissociation energies.

4 Conclusions

The influence of the exchange-correlation potential on the non-interacting kinetic energy is of the order of a few Hartree for total energies. Compared to other effects, like for example the kinetic correlation contribution, the direct influence of the functional choice has a rather large influence. Moreover, the mutual dependence of the kinetic and the exchange-correlation functional significantly influences bond distances (beyond weighted averages) and the virial ratio. Therefore, the chosen exchange-correlation functional type must be considered in the design of orbital-free density based approximations for the kinetic energy in order to assure the reproducibility of the performance.

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